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ORIGINAL ARTICLE

Diocanol; one new phenol derivative isolated and characterized from *Urtica dioica*

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KEYWORDS

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Abstract One new benzene derivative Diocanol(1) was isolated from the ethyl acetate soluble portion of the whole plant of *Urtica dioica* along with known constituents β-amyrin (2), β-sitosterol (3), stigmasterol (4), and oleanolic acid (5). The structures of the isolated compounds were characterized based on ^{1}H and ^{13}C NMR spectra, including two-dimensional NMR techniques like COSY, HMQC, and HMBC and compared with the literature data.

1. Introduction

Urtica dioica (stinging nettle) belongs to the family Urticaceae and is native to Eurasia, and is considered as a therapeutic source. Species of the genus *Urtica* usually prefers to grow in wet, rich soil and in large patches. The plant parts such as the leaf, flower, seed and root of the nettle are utilized in different ways and have different chemical constituents (Thorne Research, 2007). *Urtica dioica* is medicinally a very important plant and is used extensively in pharmaceutical formulations and is also used by local practitioners for a variety of human ailments (Iqbal et al., 2011). *Urtica dioica* herbs are utilized to care for stomach ache in Turkish folk medicine. Additionally, this herb is utilized to treat rheumatic pain and for colds and cough and is used against liver insufficiency. Aqueous infusions of Mediterranean herbs including *Urtica dioica*, exhibit antioxidant activity toward iron-promoted oxidation of phospholipids, linoleic acid, and deoxyribose (Ilhami et al., 2004). *Urtica dioica* can also be used to treat Anti-inflammatory effects (Mittman, 1990). Further accurate experiments are required to confirm this finding. Nettle leaf has usually been used for gout, hair loss, and mild bleeding, although confirmatory clinical trials have not been conducted (Grieve, 1971). These medicinal properties provoked us to perform phytochemical investigation on *Urtica dioica*. Our current study has led to the isolation of one new benzene derivative (1), along with known compounds β-amyrin (2) (Heupel, 1985), β-sitosterol (3) (Habib et al., 2007), stigmasterol (4) (Habib et al., 2007) and oleanolic acid (5) (Akuta and Itokawa, 1988). Their structures have been identified by extensive spectral methods including 1D, 2D NMR and MS. This paper deals with the isolation and structural elucidation of the new compound **1** (Fig. 1).

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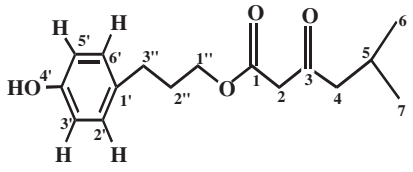

Figure 1 Structures of compound **1**.

2. Experimental

2.1. General

Column chromatography (CC) utilized silica gel, 70–230 mesh. Flash chromatography was carried out using silica gel 230–400 mesh. Thin layer chromatography (TLC) was performed with pre-coated silica gel G-25-UV-254 plates and detection was achieved at 254 nm, and by spraying with ceric sulfate in 10% H_2SO_4 solution. The IR and UV spectra were recorded on a Jasco-320-A and Hitachi-UV-240 spectrophotometers, respectively. Optical rotations were measured on a Jasco-DIP-360-digital polarimeter using a 10 cm cell-tube. Mass spectra (EI- and HR-EI-MS) were measured in an electron impact mode on either Finnigan MAT 12 or MAT 312 spectrophotometer; ions are presented in *m*/*z* (%). The ^{1}H- and ^{13}C NMR spectra were recorded on a Bruker AMX-400 spectrometer in $CDCl_3$. 2D-NMR spectra were obtained using a Bruker AMX-400 spectrometer. Chemical shifts, in parts per million (δ), relative to tetramethyl silane (TMS) as internal standard, and scalar couplings (*J*) were reported in Hertz.

2.2. Plant material

Whole parts of *Urtica dioica* were collected from Peshawar KPK Pakistan in July 2008 and identified by the help of plant taxonomist Professor Ijaz GPGC Kohat. A voucher specimen (Ud01) was deposited in the herbarium of the Botany Department of Peshawar University.

2.3. Extraction and compound isolation

The whole plant of *U. dioica* was dried in the shade, chopped and ground to coarse powder. The powdered plant (3 kg) was initially extracted with methanol for 25 days at room temperature. The methanolic extract was evaporated under reduced pressure to give 300 g residue. A portion of this (300 g) was partitioned between n-hexane, chloroform, ethyl acetate, n-butanol and water. 90 g ethyl acetate was chromatographed over a silica gel column. Elution was carried out with a gradient of increasing polarity of ethyl acetate in n-hexane up to 100% ethyl acetate, and then a gradient of methanol in ethyl acetate up to 100% methanol. Fraction A was obtained through elution with n-hexane/ethyl acetate (1:1) and was subjected to CC with n-hexane/ethyl acetate. This fraction afforded compound **1** on elution with ethyl acetate/n-hexane (2:8). Compounds **2**–**5** were obtained from fraction B in polarity ranges of 30%, 36%, 40%, 44% and 50% respectively of ethyl acetate/n-hexane.

2.4. Spectral data of compound (*1*)

Physical appearance: Amorphous solid, Amount; 12 mg. IR (KBr): (OH) 3470, (Benzene) 1740, 1510 UV λmax (MeOH) nm (log ε): 280 (5.2). ^{13}C NMR (75 MHz, CDCl3) δ: 178 (C-1), 31.9 (C-2), 204.0 (C-3), 13.6 (C-6,7), 178 (C-1), 138.1 (C-1′), 130.1 (C-2′), 115.3 (C-3′), 143.0 (C-4′), 115.3 (C-5′), 130.1 (C-6′), 62.4 (C-1″) ^{1}H NMR (300 MHz, CDCl3) δ: 4.27(2H, s, H-2), 2.91(2H, t, J = 10.3, H-4), 0.91(6H, d, J = 7.0, H-6,7), 4.06 (2H, t, J = 7.0, H-1″), 2.81(2H, m, H-2″), 2.51(2H, t, J = 7.5, H-3″), 6.52 (1H, d, J = 8.3, H-2′, 6′), 6.73 (1H, d, J = 8.3, H-3′, 5′).

3. Results and discussion

Compound **1** (Fig. 1) was isolated in amorphous solid form from the ethyl acetate extracts of *Urtica dioica*. The polarity of TLC system was ethyl acetate: hexane (2:8). This compound was UV active. The EI-MS of compound (**1**) demonstrated a molecular ion peak at m/z 278.9, while HR-EI-MS illustrated a molecular ion peak at *m*/*z* 278.9 consistent with the molecular formula $C_{16}H_{22}O_4$.

In addition to the molecular ion peak, the other high up signals emerged at *m*/*z* 44, 58, 107 and 121 (Fig. 2). Another prominent peak at 42 suggested the *McLafferty rearrangement*. Its IR spectrum displayed peaks in the region of 1740 and 1510 cm^{-1} showing the presence of a carbonyl group and benzene functionalities in the molecule. The ^{1}H NMR of compound (**1**) displayed 2 CH_3 peaks at δ 0.9 (6H, d, H-7, H-8), one oxygenated methylene at δ 4.06 (2H, t, J = 6.2 Hz), five methylenes at δ 4.27 (2H, s, H-2), 2.26 (2H, t, J = 10.3 Hz, H-4), 1.46 (2H, m, H-5), and one methine at δ 2.95 (1H, m, H-6). The ^{13}C NMR spectrum corroborated the existence of 16 signals identified as those of 2 methyls, 5 methylenes, 5 methines and 4 quaternary carbons on the basis of the DEPT experiment. The down field signal at δ 178.1 and 204.0 were assigned to two carbonyl carbons. The methylenic carbon signals at δ 33.5 and δ 22.0 were assigned to 4-C and 5-C, respectively. A rather downfield signal at δ 55.2 was assigned to C-2 between the two carbonyl carbons. An upfield signal at δ 13.6 was assigned to the two terminal methyl carbons (C-7 and C-8) respectively. The signal at δ 58.5 was assigned to '1-C [9]. The ^{1}H and ^{13}C NMR chemical shifts of methylene (δ 4.23 and 64.8) revealed its attachment with an oxygen atom. The signals at δ 62.4 and 35.2 in the ^{13}C NMR spectrum were ascribed to (C-1″) and (C-2″).

The appearance of two doublets in the aromatic region at δ 7.07 and 6.75 (J = 8.3 Hz) each having two protons integra-

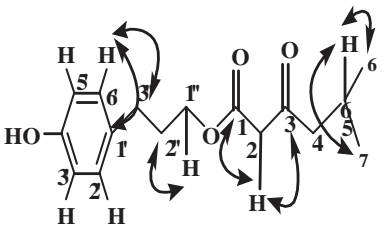

Figure 2 HMBC correlation shown of compound (1).

Table 1 ^{13}C NMR data of compound (**1**).

C. No.	Multiplicity (DEPT)	^{13}C NMR (δ)	C. No.	Multiplicity (DEPT)	^{13}C NMR (δ)
1′	C	138.1	1	C	178.1
2′	CH	130.1	2	CH_2	31.9
3′	CH	115.3	3	C	204.0
4′	C	143.0	4	CH_2	33.5
5′	CH	115.3	5	CH	42.0
6′	CH	130.1	6	CH_3	13.6
1″	CH_2	62.4	7	CH_3	13.6
2″	CH_2	35.2			
3″	CH_2	34.3			

Table 2 ^{1}H NMR data of compound **(1).**

Position	^{1}H NMR (δ)/Multiplicity	Coupling Constant J(Hz)	Position	^{1}H NMR (δ)/Multiplicity	Coupling Constant J(Hz)
1	–	–	1″	4.06 t	7.0
2	4.27 s	–	2″	2.81 m	–
3	–	–	3″	2.51 t	7.5
4	2.21 d	10.3	1′	–	–
5	1.44 m	–	2′, 6′	6.52 d	8.3
6–7	0.91 d	7.0	3′, 5′	6.73 d	8.3
			4′	–	–

tion with the same coupling constant (J = 8.3 Hz) indicated a para substitution pattern. The doublets at δ 7.07 and 6.75 were found to associate with the carbons at δ 130.0 and 115.3, respectively through HMQC experiments and were considered as methines with the help of DEPT experiments. The CH signal at 130.0 was assigned to the ortho positions (C-2′, C-6′). C-3′ and C-5′ were automatically awarded by the methines at δ 115.3 having protons at δ 6.7. The quaternary signal at δ 130.1 was assigned to C-1′ with the help of the literature values. The chemical shift value δ 154.2 of a quaternary signal revealed its connection to a OH group and was allotted to C-4′ at δ 7.0 (H-2′, H-6′). The ^{1}H NMR of compound **2** demonstrated four more signals, a singlet at δ 4.2(C-2), a triplet at δ = 1. 9 (C-4, J = 7.6 Hz), a multiplet at δ 1.3 (C-5) and an upfield triplet at δ 0.9 (C-6, J = 7.1 Hz), having integration of two and three protons, respectively. All the chemical shifts were verified through ^{13}C NMR, ^{1}H NMR, EI, and HMBC (Fig. 2). The argument so far guided us to the alloted compound (**1**) 3″-(4′-hydroxyphenyl) propyl-3-oxo-heptanoate. The ^{13}C NMR and ^{1}H NMR chemical shifts of compound (**1**) are presented in Tables 1 and 2, respectively.

4. Conclusion

One new benzene derivative (1) along with known constituents β-amyrin, β-sitosterol, stigmasterol and oleanolic acid were isolated from *Urtica dioica*.

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References

Akuta, A., Itokawa, H., 1988. Triterpenoids of Paeonia japonica callus tissue. Phytochemistry 27, 2813–2815.

Grieve, M.A., 1971. In: Modern Herbal, vol. 2. Dover Publications, New York, NY, pp. 574–579.

Habib, M.R., Nikkon, F., Rahman, M., 2007. Isolation of stigmasterol and beta sitosterol from methanolic extract of root of bark of *Calotropis gigantean* (Linn.). Pak. J. Biol. Sci. 10, 4174–4176.

Heupel, R.C., 1985. Varietal similarities and differences in the polycyclic isopentenoid composition of sorghum. Phytochemistry 24, 2929–2937.

Ilhami, G., Irfan, K.O., Oktay, M., Buyukokuroglu, M.E., 2004. Antioxidant, antimicrobial, antiulcer and analgesic activities of nettle (*Urtica dioica* L.). J. Ethnopharmacol. 90, 205–215.

Iqbal, H., Moneeb, U.R.K., Zia Riazullah, M., Naeem, K., Farhat, A.K., Zahoor, U., Sajjad, H., 2011. Phytochemicals screening and antimicrobial activities of selected medicinal plants of Khyberpakhtunkhwa Pakistan. Afr. J. Pharm Pharmacol. 6, 746–750.

Mittman, P., 1990. Randomized double-blind study of freeze-dried *Urtica dioica* in the treatment of allergic rhinitis. Planta Med. 56, 44–47.

Thorne Research., 2007. Inc. Alternative Medicine Review, 12(3).